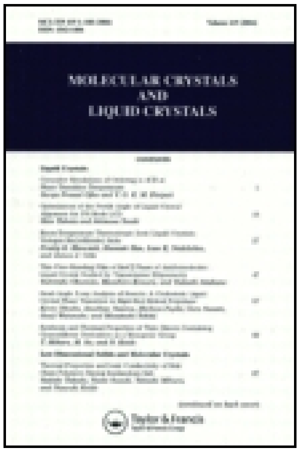

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Sneŝ Půek [a] , A. Kadashchuk [b] , N. Ostapenko [b] & V. Zaika [b]

[a] Institute of Macromol. Chem., AS., 162 06, Prague 6, Czech Republic

[b] Institute of Physics NAS, Kiev-22, Ukraine

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Relation Between Thermoluminescence and Charge Transport in Polysilylenes

S.NEŠPŮREK[a)], A.KADASHCHUK[b)], N.OSTAPENKO[b)], V.ZAIKA[b)]
[a]Institute of Macromol. Chem., AS,. 162 06 Prague 6, Czech Republic;
[b]Institute of Physics, NAS, Kiev-22, Ukraine

The low-temperature thermally stimulated luminescence (TSL) has been applied for probing the energetic disorder of localized states in poly(methyl-phenylsilylene) (PMPSi). Interpretation of TSL as associated with charge carrier thermal release from intrinsic tail states and based on the Gaussian disorder model is suggested. The analysis the shape of the high-temperature wing of the TSL peak yields the half-width of the density of states (DOS) profile that agrees with energetic disorder parameter determined from the post-transient part of the transient photocurrent. The activation energy in TSL peak maximum is in accord with predictions of the theory for non-activated energetic relaxation of charge-carriers within a manifold of localized states and, therefore, no special features of the DOS in the gap are necessary for the explanation of the existence of the TSL peak. The effect of polar additives as dinitrobenzenes is explained in terms of dipolar disorder model.

Keywords: disordered molecular solid, thermoluminescence, charge transport, dipolar disorder, poly(methyl-phenylsilylene)

INTRODUCTION

The charge transport in poly(methyl-phenylsilylene) (PMPSi) has been believed to be controlled by charge hopping through intrinsic states derived from domain-like segments of the silicon chain and interpreted in terms of Gaussian disorder model of Bässler [1] assuming the distribution of the (DOS) function of the Gaussian shape. In the present work we use the low-temperature thermally stimulated luminescence (TSL) for probing the energetic disorder of localized states in PMPSi, combining the results of these TSL studies and charge transport properties. Our approach [2,3] is based on the assumption that the lowest portion of the DOS at very low temperatures may behave as traps for charge carriers. Therefore, by analyzing the trap distribution function, one may estimate the shape of the deepest part of the DOS and, consequently, the parameter of the energetic disorder - the half-width of the DOS, σ.

EXPERIMENTAL

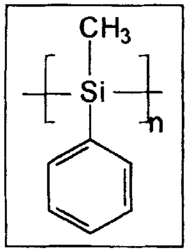
TSL, after UV-light excitation of samples, was measured over the range 4.2-300 K both under the uniform heating with the rate 0.15 K/s and in the fractional heating regime [4]. The fractional TSL, being an extension of the initial rise method, is based on cycling of the sample temperature (see inset in Fig. 1a) superimposed on a uniform heating. It enables the determination of the mean activation energy, <E>, and trap distribution function, H(E), of the trapped charge carriers. The basic relations are:

$$\langle E \rangle = -d(\ln I)/d(1/kT), \qquad (1)$$

where I is the intensity of the TSL, T is the sample temperature, and k is the Boltzmann constant;

$$H(E) \sim I(T)/(d\langle E \rangle/dT). \qquad (2)$$

Scheme 1



Poly(methyl-phenylsilylene) (PMPSi, see Scheme 1) was prepared by Wurtz coupling polymerization, as described by Zhang and West [5]. Thin films for TSL measurements (thickness about 3 μm) were spin-coated from a toluene solution on stainless steel substrates.

RESULTS AND DISCUTION

PMPSi have shown a strong TSL induced by UV radiation. Figure 1a presents the typical TSL glow curve of PMPSi film (curve 1)

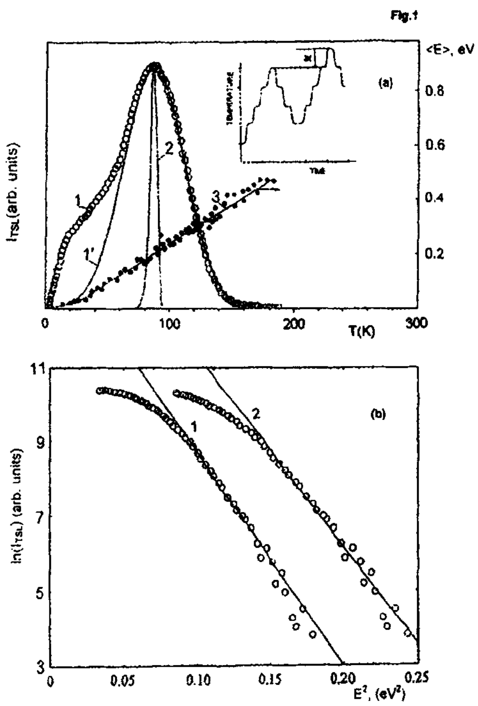


FIGURE 1 (a) TSL glow curve under excitation at 4.2 K for PMPSi and its Gaussian fitting (curve 1 and 1', respectively); calculated TSL peak obtained according to discrete trap model (curve 2). Temperature dependence of the <E> (curve 3); extrapolation by Eq. 3 is given by solid line.
(b) Gaussian analysis of the high-energy wing of the TSL peak when used the Eq.3 (curve 1) and the Eq.4 (curve 2). Lines 1 and 2 are fitting with $\sigma' = 0.094$ and 0.0985 eV, respectively.

As one can see, the TSL glow curve shows a broad peak with a maximum at ≈85 K. The existence of a quasi-continuous trap distribution in PMPSi has been found. The mean activation energies, <E>, linearly increases with temperature (Fig. 1a, curve 3) according to the empirical formula (in eV)

$$\langle E\rangle(T) = 0.0028\times T - 0.05 \qquad (3)$$

The activation energy and frequency factor in the maximum of TSL glow curve is $<E_m>=0.19$ eV and $S \cong 10^{10}$ s^{-1}, respectively.

The parameter of the energetic disorder of PMPSi, $\sigma=0.093$ eV [6], was determined by attributing the entire temperature dependence of the charge mobility to disorder. Recently it was demonstrated [7] that although the disorder is still the major contributor, charge transport in PMPSi is governed by a superimposition of a disorder and polaron effect, the polaron binding energy being 0.16 eV. The true width of the DOS was estimated as $\sigma = 0.078$ eV.

Let us assume that the TSL of PMPSi is associated with thermal release of charge carriers occupying the tail sites of the DOS distribution of a Gaussian shape. Note, that in the case of the linear temperature dependence of $<E>(T)$ (cf. Eq. 3), the expression (2) [4] predicts that the temperature profile of the TSL peak should directly reflect the trap distribution function, H(E). The result of a Gaussian analysis converting the temperature scale to the trap energy scale using the empirical calibration formula (3), is presented in Fig. 1b, curve 1. The following conclusions can be drawn from the above analysis: (i) The high-energy wing of TSL peak can be well approximated by Gaussian distribution; (ii) The half-width of this distribution, σ', formally determined from the slope, yields $\sigma' = 0.094$ eV (Fig.1b, solid line 1). This value reasonably agrees with $\sigma = 0.093$ eV [6] discussed above.

It should be mentioned that the above analysis should be corrected taking the existence so called transport energy, E^*, into account. This energy is normally located below the center of the DOS [8] and is defined as $E^* = -\sigma$ [8] for the Gaussian shape of DOS. To do that, to zero approximation, one can modify Eq.3 by adding the E^* value, i.e. 0.078 eV:

$$<E>(T) = (0.0028\times T - 0.05) + 0.078 \qquad (4)$$

The modified Gaussian analysis of TSL peak using Eq. (4) instead of (3) is presented in Fig.1b (curve 2) and yields the value of $\sigma'=0.0985$ eV which is only slightly larger than that extracted from curve 1.

This approach is supported by the comparison of the activation energy at the maximum of the TSL peak and the mean energy of the charge carrier packet ΔE (relative to the center of the DOS), as predicted by the theory for non-activated energetic relaxation of particles within the DOS with Gaussian distribution in energy at zero-temperature [9]: $\Delta E = -\sigma\,[3\ln\ln(t/t_0)]^{1/2}$, where t is the time and t_0 is equal to 10^{-13} s [1]. Assuming $\sigma = 0.09$ eV and the typical value of the experiment $t = 10^2$ s, the calculated value is $\Delta E = 0.29$ eV which agrees with experimental value of activation energy 0.27 eV (Eq. 4).

In the final part we present the effect polar additives - dinitrobenzenes (DNBs), both on TSL and charge transport in PMPSi. The influence of p-, m-, and o-DNB (dipole moments are 0, 3.8, and 6 D, respectively) on charge carrier mobility is shown in the insert of Fig.2. As one can see, the higher dipole moment of an additive, the lower is the mobility. This effect can be explained in terms of dipolar disorder [6,10] as due to an increase in σ - the energy distribution of charge-transporting states is broadened by the electrostatic interaction of charge carriers with static dipoles of the additive. A similar effect was found by TSL measurements of these systems, which manifests itself in a broadening the high-temperature wing of the TSL peak. The Gaussian analysis of the relevant TSL peaks is presented in Fig.2, and clearly demonstrates an increase of disorder parameters (derived from the slopes of the plots) upon the addition of polar DNB with c=0.5%: $\sigma'=0.085$, 0.103 and 0.117 eV for p-, m- and o-DNB, respectively (here the transport energy concept was not considered). The presented TSL data (Fig.2) are in good aggrement with the observed reduction of the charge mobility in PMPSi.

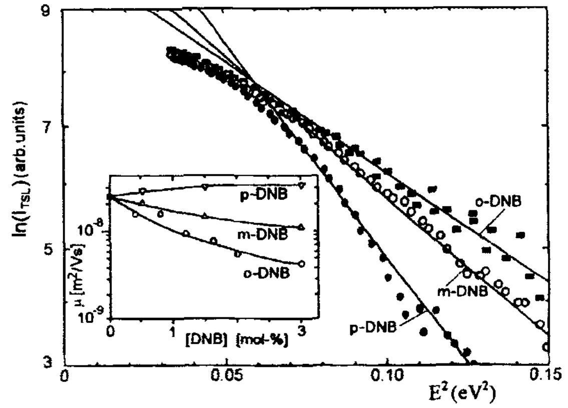


FIGURE 2. Gaussian analysis of TSL peaks of PMPSi containing polar additives (0.5%): p-, m-, and o-DNB (slopes of solid lines yield σ' = 0.085, 0.103 and 0.117 eV, respectively). The insert show the influence of DNBs on charge mobility in PMPSi.

Acknowledgments

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